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In a recent letter [1], Samanta, Musharaf Ali and Ghosh set out to understand the low density failure of the entropy scaling law for the self-diffusion coefficient D conjectured by Dzugutov [2] and to provide a simple alternative. After an interesting derivation, that however contains a number of uncontrolled approximations, they arrive at Eq. 7 of [1], which reduces for a hard sphere fluid to:

$$\frac{D}{D_E} = \frac{A}{1 - s_e/k_B} \tag{1}$$

where $D_E = D_B/\chi$ is the Enskog diffusion coefficient [3], $D_B = 3(k_BT/\pi m)^{\frac{1}{2}}/8\rho\sigma^2$ the Boltzmann diffusion coefficient, χ the contact value of the pair correlation function, s_e the excess entropy per particle, and A a constant that the authors set to 2.5. Using the excess entropy $s_e/k_B = -(4\eta - 3\eta^2)/(1-\eta)^2$ and contact value $\chi = (2-\eta)/2(1-\eta)^3$ obtained from the Carnahan-Starling equation of state [4] ($\eta = \pi\rho\sigma^3/6$ - packing fraction), we test this relation against the hard sphere molecular dynamics simulation results of Erpenbeck and Wood (EW)[5] - Fig. 1. The disagreement is quite significant and more important the behavior of the two curves is very different, as $(D/D_E)_{EW}$ is not a monotonically decreasing function of $(-s_e/k_B)$. The discrepancy cannot be attributed to the authors use of an approximation for the excess entropy.

The idea of entropy scaling for transport coefficients has a fairly long history [6]. Arguing on the basis of the molecular "caging" effect Dzugutov [2] proposed the scaling law:

$$\frac{D}{\sigma^2\Gamma_E} = B\exp\left(s_e/k_B\right) \tag{2}$$

which assumes that the natural length and time scales for diffusion are given by a suitably defined hard sphere diameter σ and the Enskog collision frequency $\Gamma_E = 4\sigma^2\chi\rho\sqrt{\pi k_BT/m}$, with B an universal constant. Unfortunately, the above relation appears to work only in a limited, high density domain for both hard spheres [7] and realistically modeled fluids [8]. The problem that arises at low and moderate densities (see Fig. 1) with the scaling introduced in Eq. 2 can be understood if we observe that the left-hand-side of that equation can be written up to a multiplicative constant as $D/D_B\chi\eta^2$. Therefore, in the limit of a dilute system, $\eta \to 0$, this term diverges as $1/\eta^2$, while the right-hand-side of Eq. 2 remains finite. This behavior should be expected for any valid definition of σ and χ and s_e approximation.

The noted pathology of Eq. 2 can be avoided by replacing σ as the relevant length scale with $1/\rho\sigma^2$, the Boltzmann mean-free path, which should be a reasonable measure of the degree of molecular confinement, $1/\rho\sigma^2 \propto \sigma/\eta$. The new relationship is:

$$\frac{D}{D_B\chi} = \exp\left(\gamma s_e/k_B\right) \tag{3}$$

where we introduced a different constant γ. The test of this suggested dependence is shown in Fig. 2 for hard spheres, with $\gamma = 0.8$. Furthermore, Eq. 3 holds for Van der Waals fluids as well when a reasonable definition for σ is used [8].

Samanta et al. also propose a generalized Stokes-Einstein relation connecting the diffusion coefficient and the viscosity. It is worth pointing out that such a relation is hardly necessary given that the usual Stokes-Einstein relation with the 'slip' boundary condition holds well for both hard spheres [9] and Van der Waals fluids [8].

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[1] A. Samanta, Sk. Musharaf Ali, S.K. Ghosh, Phys. Rev. Lett. **92**, 145901 (2004).

[2] M. Dzugutov, Nature(London) **381**, 137 (1996).

[3] S. Chapman, T.G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, Cambridge, England, 1970).

[4] J.-P. Hansen, I.R. McDonald, *Theory of Simple Liquids*, 2^{nd} edition, (Academic Press, London, 1986).

[5] J.J. Erpenbeck, W.W. Wood, Phys. Rev. A **43**, 4254 (1991).

[6] Y. Rosenfeld, Phys. Rev. A **15**, 2545 (1977).

[7] E.G.D. Cohen, L. Rondoni, Phys. Rev. Lett. **84**, 394 (2000).

[8] S. Bastea, Phys. Rev. E **68**, 031204 (2003).

[9] B.J. Alder, D.M. Gass, T.E. Wainwright, J. Chem. Phys. **53**, 3813 (1970).

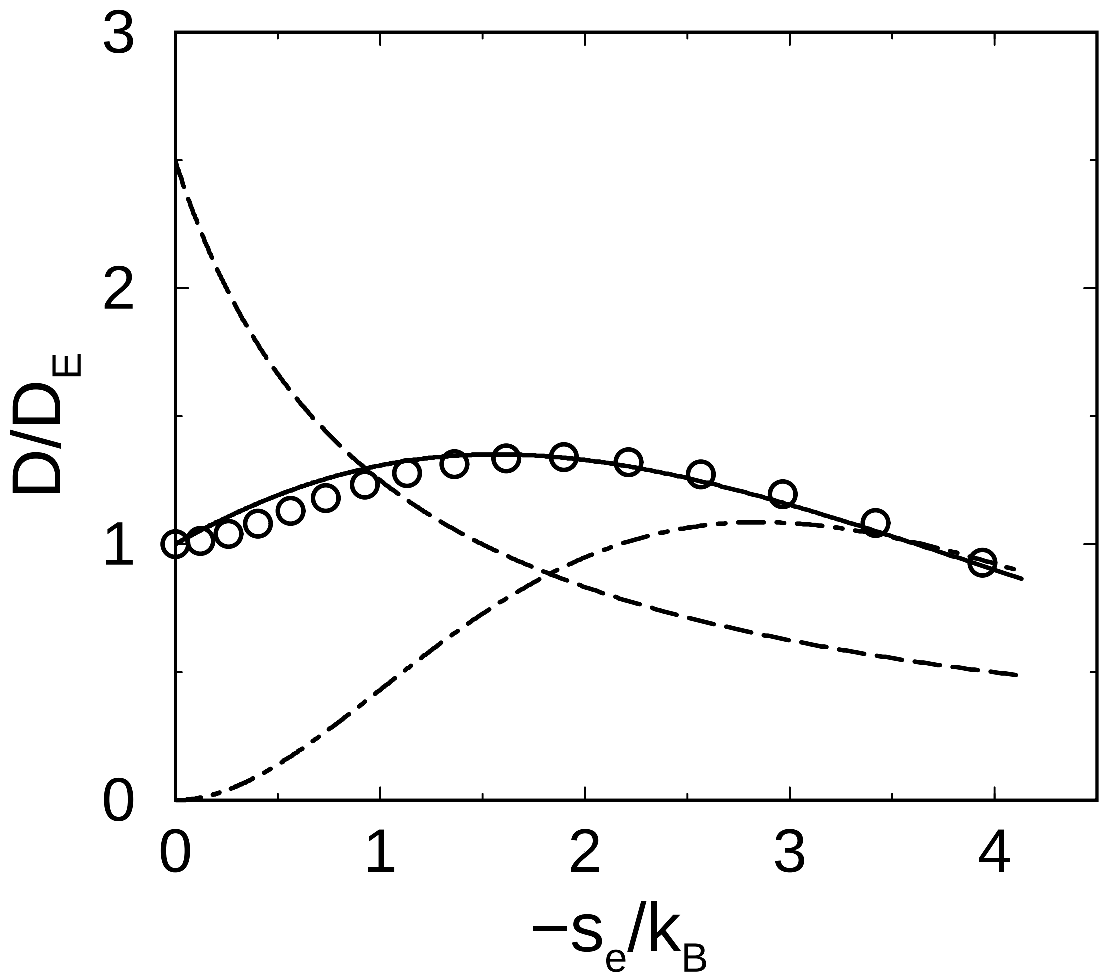

FIG. 1: Comparison of the hard spheres diffusion coefficient (simulation results of Ref. [5]) - circles, with the scaling relation proposed by Samanta et al. [1] (Eq. 1) - dashed line, Dzugutov scaling law [2] (Eq. 2) - dot-dashed line, and new entropy scaling (Eq. 3) - solid line.